AMENDMENT
(Amendment by regulation of Article 11 of the Law)

To : Mr. Kenichi Ohashi, Examiner of the Patent Office

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1. Identification of the International Application
PCT／JP03／04435

2. Applicant
Name: Japan Science and Technology Agency
Address: 1-8, Hon-cho, 4-chome, Kawaguchi-shi,
Saitama 332-0012 JAPAN
Country of nationality: JAPAN
Country of residence: JAPAN

3. AGENT
Name: HIRAYAMA, Kazuyuki
Patent Attorney (8287)
Address: 6th Floor, Shinjukugyoen Bldg.
3-10, Shinjuku 2-chome, Shinjuku-ku,
Tokyo 160-0022 JAPAN

4. The Objects of Amendment
Specification, Claims, and Figures

5. Content of Amendment
(1) English Specification, p.3, paragraph [0007] Line 9:
"(Composition formula: $Ce_{1-x}Pr_xO_{2-x/2}$)" is amended as
"(Composition formula: $Ce_{1-x}Pr_xO_{2-x/2}$, where $0<x<0.5$)".

(2) English Specification, p.11, paragraph [0024] Line 6 :
"$(Ce_{0.8}Gd_{0.2})O_2$" is amended as "$(Ce_{0.8}Gd_{0.2})O_{1.9}$".

(3) English Specification, p.11, paragraph [0024] Line 7:

"$(Ce_{0.8}Pr_{0.2})O_2$" is amended as "$(Ce_{0.8}Pr_{0.2})O_{1.9}$".

(4) English Specification, p.11, paragraph [0024] Line 9:
"$(Ce_{0.8}Gd_{0.2})O_2$" is amended as "$(Ce_{0.8}$ $Gd_{0.2})O_{1.9}$".

(5) English Specification, p.11, paragraph [0024] Line 10:
"$(Ce_{0.8}Pr_{0.2})O_2$ – 15M" is amended as "$(Ce_{0.8}Pr_{0.2})O_{1.9}$ – $15MnFe_2O_4$".

(6) English Claims, p.15, Claim 2:
"(Composition formula: $Ce_{1-x}Pr_xO_{2-x/2}$)" is amended as
"(Composition formula: $Ce_{1-x}Pr_xO_{2-x/2}$, where $0<x<0.5$)".

(7) Fig.6 of the attached figures is changed with the newly drawn version attached here.

6. List of Attached Documents
   (1) New English Specification, p.3, p.11:
   (2) New English Claim, p.15:
   (3) New Fig.6:

Eur. Ceram. Soc. 21, 2001, 1763.).

[0006] In view of the above-mentioned problems, it is the first object of the present invention to provide a composite-type mixed oxygen ion and electronic conductor, in which oxygen ion conductive phase and electronic conductive phase are uniformly mixed, thereby cracking due to the difference of thermal expansion coefficient does not occur, oxygen ion conductive phase and electronic conductive phase respectively form conductive networks, and a different phase to disturb mixed conductivity is not formed by the reaction of both phases, consequently oxygen permeability is high, and aged deterioration does not easily occur. In addition, it is the second object to provide the method to manufacture said composite-type mixed oxygen ion and electronic conductor.

Disclosure of the Invention

[0007] In order to attain the above-mentioned objects, a composite-type mixed oxygen ion and electronic conductor of the present invention is characterized in that it comprises gadolinium-doped cerium oxide (composition formula: $Ce_{1-x}Gd_xO_{2-x/2}$, where $0<x<0.5$) as oxygen ion conductive phase, and spinel-type ferrite (composition formula: MFe_2O_4, where M=Mn, Fe, Co, Ni) as electronic conductive phase.

Also, another composite-type mixed oxygen ion and electronic conductor of the present invention is characterized in that it comprises praseodymium-doped cerium oxide(Composition formula: $Ce_{1-x}Pr_xO_{2-x/2}$, where $0<x<0.5$) as oxygen ion conductive phase, and spinel-type ferrite (composition formula: MFe_2O_4, where M=Mn, Fe, Co, Ni) as electronic conductive phase.

[0008] In the above composite-type mixed oxygen ion and electronic conductors of the present invention, oxygen ion conductive phase may contain a catalyst or catalysts to accelerate conversion of oxygen gas to oxygen ion, and oxygen ion to oxygen gas, or it is coated with catalysts on the surface of oxygen ion conductive phase to accelerate conversion of oxygen gas to oxygen ion, and oxygen ion to oxygen gas.

In the composite-type mixed oxygen ion and electronic conductor of the present invention, oxygen ion conductive phase and electronic conductive phase respectively may consist of fine particles having a diameter of 1 μ m or less, the respective phases are mutually mixed uniformly, and form the

oxygen ion conductive phase GDC. Also 25LSM is the composite-type mixed conductor in which the electronic conductive phase LSM expressed by the composition formula $(La_{1-x}Sr_x)MnO_3$ was mixed by 25% by volume ratio into oxygen ion conductive phase GDC.

[0024] Fig.6 is a graph showing oxygen permeation coefficient of the composite-type mixed oxygen ion and electronic conductor of the present invention. The oxygen permeation coefficient used here is the value obtained by multiplying the oxygen permeation flux density with the sample thickness L, and one of the index of permeability not dependent on the film thickness. The measured samples were $(Ce_{0.8}Gd_{0.2})O_{1.9}$ – 15vol%$MnFe_2O_4$ and $(Ce_{0.8}Pr_{0.2})O_{1.9}$ – 15vol%$MnFe_2O_4$. In the figure, the ordinate shows the oxygen permeation coefficient, and the abscissa shows the temperature. △ shows the oxygen permeation coefficient of $(Ce_{0.8}Gd_{0.2})O_{1.9}$ – 15vol%$MnFe_2O_4$, and ○ shows the oxygen permeation coefficient of $(Ce_{0.8}Pr_{0.2})O_{1.9}$ – 15$MnFe_2O_4$.

From the figure, it can be seen that the composite-type mixed conductor with praseodymium-doped cerium oxide as an ionic conductive phase has higher oxygen permeation coefficient than that with gadolinium-doped cerium oxide as an ionic conductive phase. Here, since the price is lower for Pr than Gd, the composite-type mixed conductor with praseodymium-doped cerium oxide as an ionic conductive phase is quite useful in industry use.

[0025] Next, explanation will be given concerning to the volume composition ratio of an electronic conductive phase to an oxygen ion conductive phase.

Fig.7 is a graph showing the dependency of the oxygen permeation coefficient upon the volume ratio of the electronic conductive phase to the ionic conductive phase of the composite-type mixed oxygen ion and electronic conductor of the present invention. The samples used for measurement had GDC as an oxygen ion conductive phase, and $MnFe_2O_4$ as an electronic conductive phase. The abscissa shows the volume ratio x of $MnFe_2O_4$ phase to GDC phase, and the ordinate shows oxygen permeation coefficient. The measurement temperatures were 800℃, 900℃, and 1000℃.

As is seen from the figure, the oxygen permeation coefficient being usable is attained from x = 5%, and it rapidly decreases with x = 40% or more as seen in the graph of 1000℃. Consequently, the preferable volume composition ratio of the electronic conductive phase to the oxygen ion conductive phase is in the range of 5% – 40%.

The Claims

What is claimed is:

1. A composite-type mixed oxygen ion and electronic conductor, characterized in that its oxygen ion conductive phase consists of gadolinium-doped cerium oxide (composition formula: $Ce_{1-x}Gd_xO_{2-x/2}$, where $0<x<0.5$), and its electronic conductive phase consists of spinel-type ferrite (composition formula: MFe_2O_4, where M=Mn, Fe, Co, or Ni).

2. (Amended) A composite-type mixed oxygen ion and electronic conductor, characterized in that its oxygen ion conductive phase consists of praseodymium-doped cerium oxide(Composition formula: $Ce_{1-x}Pr_xO_{2-x/2}$, where $0<x<0.5$), and its electronic conductive phase consists of spinel-type ferrite (composition formula: MFe_2O_4, where M=Mn, Fe, Co, or Ni).

3. A composite-type mixed oxygen ion and electronic conductor as set forth in claim 1 or 2, characterized in that said oxygen ion conductive phase contains a catalyst or catalysts to accelerate conversion of oxygen gas to oxygen ion or oxygen ion to oxygen, or is coated with said catalysts, or contains said catalysts and coated with said catalysts on the surface.

4. A composite-type mixed oxygen ion and electronic conductor as set forth in claim 3, characterized in that said catalyst is Ru or Ni, or their combination.

5. A composite-type mixed oxygen ion and electronic conductor as set forth in any one of claims 1 to 4, characterized in that said oxygen ion conductive phase and said electronic conductive phase, respectively consists of fine grains having diameter of 1 μm or less, are uniformly mixed with each other, and respectively form conductive networks.

6. A composite-type mixed oxygen ion and electronic conductor as set forth in any one of claims 1 to 5, characterized in that volume composition ratio of said electronic conductive phase to oxygen ion conductive phase is in the range of 5 to 40%.